Improvements in and relating to the production of magnesium and alkali earth metals by electrolysis of fused starting materials

Publication number: GB452269
Publication date: 1936-08-19
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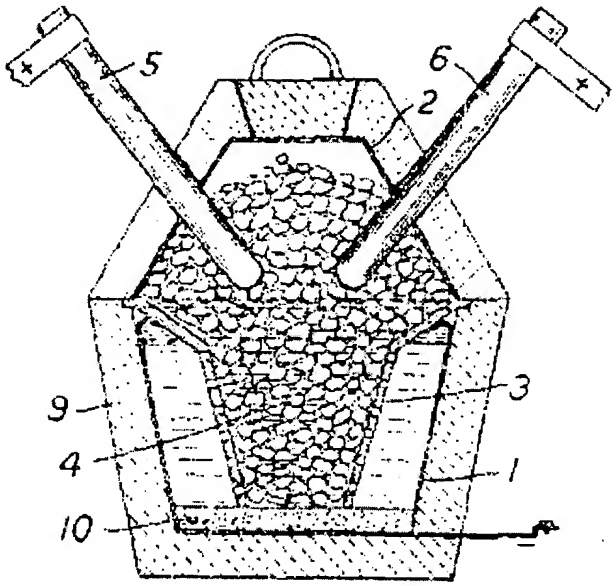
Classification:
- international: ***C25C7/02;*** **C25C7/00;**
- European: C25C7/02D
Application number: GB19360006923 19360307
Priority number(s): ATX452269 19350313

Abstract of **GB452269**

452,269. Electrolytic production of magnesium and alkaline earth metals. MAGALL AKT. - GES., 14, Rieterstrasse, Zurich, Switzerland. March 7, 1936, No. 6923. Convention date, March 13, 1935. [Class 41] The metals are obtained by electrolysis of their fused halides which are regenerated by reaction of the nascent halogen with anode material 4 consisting of lumps of a composition containing an intimate mixture of carbon and /or coke and /or graphite with the oxide or carbonate of the metal. The anode material is contained within a perforated funnel 3 of insulating material, and extends in a column above the electrolyte level enclosed by an iron container 2 in order to maintain good contact by pressure. Contact with the . material is made by electrodes 5, 6 which may be employed for resistance heating at starting. The cathode is constituted by a lower iron vessel 1, the base of which is covered with a rammed carbon composition 10 to prevent short - circuiting. The members 1, 2 are surrounded by lagging 9.



PATENT SPECIFICATION

Convention Date (Austria) : March 13, 1935.

452,269

Application Date (In United Kingdom) : March 7, 1936. No. 6923/36.

Complete Specification Accepted : Aug. 19, 1936.

COMPLETE SPECIFICATION.

Improvements in and relating to the production of Magnesium and Alkali Earth Metals by Electrolysis of Fused Starting Materials

We, MAGALL AKTIENGESELLSCHAFT, a Company registered under the laws of Switzerland, and having its registered place of business at 14, Rieterstrasse, Zürich, 2, Switzerland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of magnesium and alkali earth metals by electrolysis of fused starting materials.

The recovery of magnesium and alkali earth metals from magnesium and alkali earth carbonates is effected, as is well known, in two stages, the first of which comprises the production of anhydrous halide (from the carbonate) and the second the electrolysis of the fused halide in suitable furnaces.

The present process likewise has for its object a process for the production of magnesium and alkali earth metals by the electrolysis of fused starting materials wherein the halogens formed at the anode, which is in the form of pieces or lumps, react with the carbonate or oxide of magnesium or an alkali earth metal, with the formation of magnesium or alkali earth halide, but differs essentially from the processes hitherto proposed in that the carbonate or oxide of magnesium or an alkali earth metal is intimately mixed with porous carbon and/or coke and/or graphite, the resulting mass being brought into the form of pieces or lumps which serve as the anode by the provision of current leads.

Thus in the present process the recovery of the magnesium and alkali earth metal halide from the carbonate or oxide and the electrolysis of the fused halide are linked up together, so that both phases of the process can be carried out in one and the same furnace and in a single uninterrupted working stage and the halogen which is formed at the anode is not evolved in the molecular state but reacts with the carbonate or oxide of the magnesium or alkali earth metal (that is originally present) or with the oxide that is produced in the furnace) with the formation of the respective fused halides.

Whereas with the methods known before, in the production of magnesium and alkali earth halide from carbonate, to bring about a similar reaction, gaseous chlorine, that is to say Cl_2 in the molecular state, is fed in from the outside, with our process the halogen is brought to bear, immediately after the evolution at the anode, in the nascent state in which it is present in a particularly active form, namely as atomic Cl. Given suitable surface texture of the material of the anode, the halogen does not occur at all in the gaseous state. Consequently the deposition voltage of the chlorine is very considerably lowered (depolarized), so that the electrolysis can be carried out at lower voltage than with the usual methods using compact carbon anodes. Further advantages accruing from our process are that the chlorine is brought to bear free from impurities and that the danger of the furnace walls being attacked by the gaseous chlorine is eliminated.

Such a course of the reaction can be obtained by using a fragmentary anode mass of the composition hereinbefore mentioned. In order to ensure that contact is actually formed between the individual pieces of carbon in the anode mass care must be taken to ensure that the fragmentary anode mass is subjected to a certain degree of pressure. This result can be most simply achieved by heaping up the mass to an appropriate extent above the level of the salt melt in the furnace.

We have found by experience that the electric resistance of anodes of this description consisting of granular or fragmentary material is surprisingly low (a cubic meter shows a resistance of 0.1 Ohm), so that the direct transition of current to all the fragments is ensured. On the other hand the contact is inadequate when for instance carbon and MgO are introduced into the anode space and merely left to float in the melt, as described in the German specification No. 589,403 (to Camescasse) for the purpose of absorbing the chlorine gas generated at the compact anode.

In our process the electrolysis is carried

out with the fused halide, for example $MgCl_2$, or with known mixtures of this salt with alkali halides at temperatures between 650° and 800° C. with the usual bath voltage (6 to 8 Volts) and current densities of 0.1 to 10 Amps./cm².

The specific gravity of the electrolyte is not of any essential significance for the carrying out of the electrolysis.

The alkali earth or magnesium halide consumed in the electrolysis is continuously replaced with the consumption of carbonate and carbon; as with the known methods of electrolysis, the electrolytic efficiency amounts, in the case of magnesium, to 70—90%.

Our method, according to the present invention, affords the following advantages.

As initial substances for admixture with the carbon for the formation of the anode material there can be employed the carbonate or the oxide of magnesium or an alkali earth metal. The combining of the halide production and the electrolysis of the fused salt means a saving of heat, more particularly seeing that the process of halide formation is exothermic.

Through depolarization of the anode voltage the consumption of energy in the electrolysis is reduced. In consequence of the fact that the fragmentary mass of carbon and carbonate or oxide with large superficial area is alone employed as anode, and is located in a space retained at the full furnace temperature, the discharge chlorine gas at once reacts with the magnesium or alkali earth oxide with the formation of magnesium or alkali earth chloride, in contrast to the process of Camescasse in which the gaseous chlorine generated at a compact anode passes through a mixture of carbon and magnesite floating in the melt. With the latter arrrangement the desired reaction only takes place partially, while, as practical tests with this latter method have shown, on account of the low temperature at the surface of the bath, and on account of the reduced reactability of the gaseous molecular chlorine, poisonous phosgene becomes formed in accordance with the formula

$$CO + Cl_2 = COCl_2,$$

the CO being evolved in the carbon mass by reduction of the CO_2 formed from the magnesite by cleavage.

Tests have shown that with our method the formation of phosgene is avoided altogether.

The starting up of the furnace is very greatly facilitated by the fact that the anode, which is provided with two current leads and consists of a fragmentary mass of carbon and carbonate or oxide, can also be switched as an electric resistance furnace until the salt charge has become fused. By virtue of the use of a fragmentary mass of porous carbon and carbonate or oxide as previously mentioned as the material of the anode the current density conditions are rendered so favourable, in consequence of the large superficial area of the pieces, that the furnace withstands relatively very high current loads.

A form of construction of plant for carrying out the process of the present invention is shown diagrammatically, and by way of example, in the accompanying drawing.

The electrolysing furnace consists of a suitably lagged two-part iron container 1, 2 between the two halves of which there is inserted an insulating body 3 the walls of which in the funnel-shaped part 3^1 are impervious, while the lower part 3^{11} is of grid- or grating-like construction.

The chamber 4 within the inserted body 3 is filled, up to or above its upper edge, with the composition consisting of coke and carbonate or oxide constituting the anode mass in which there are buried from above two stout graphite or carbon electrodes 5 and 6 in conducting contact with the anode mass. During electrolysis the lower part of the iron container 1 is connected to the negative pole, while the two carbon electrodes 5 and 6, and therefore also the fragmentary anode material 4, are connected to the positive pole of the current source. The magnesium or alkali earth metal formed at the cathode collects, according to its specific gravity, in the upper part or at the bottom of the cathode chamber 7. The charging of the furnace is effected through the closable aperture 8. 10 denotes a cover of rammed carbon composition over the bottom of the cathode 1 in order to avoid a short-circuit.

The furnace is protected against loss of heat by a lagging 9 of refractory insulating material.

The arrangement of the furnace can also be modified as compared with that shown in the drawing, so that one or more centrally disposed cathodes are surrounded by an anode consisting of fragmentary material of the described nature.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of magnesium and alkali earth metals by electrolysis of fused starting materials, in which the halogens formed at the anode react with carbon and magnesium or alkali earth carbonate or oxide, with the

formation of magnesium or alkali earth halide, with the employment of the anode material in the form of pieces or lumps, characterized by the fact that the carbonate or oxide is intimately commixed with porous carbon and/or coke and/or graphite, the resulting mass brought into the form of pieces or lumps, and these pieces or lumps connected as anode by the provision of current leads.

2. A process as claimed in Claim 1, characterized by the fact that, for the purpose of establishing satisfactory contact, the said fragmentary anode mass is subjected to pressure by being heaped up to an appropriate extent above the level of the melt in the furnace.

3. A process as claimed in Claim 1, characterized by the fact that the said fragmentary material is provided at two or more points with current leads, in order to admit of starting up the furnace as a resistance furnace.

4. The process for the production of magnesium and alkali earth metals by electrolysis of fused starting materials substantially as described.

5. Magnesium and alkali earth metals whenever produced by the process according to any of the preceding claims.

Dated this 7th day of March, 1936.
BLACKBURN & POULETT,
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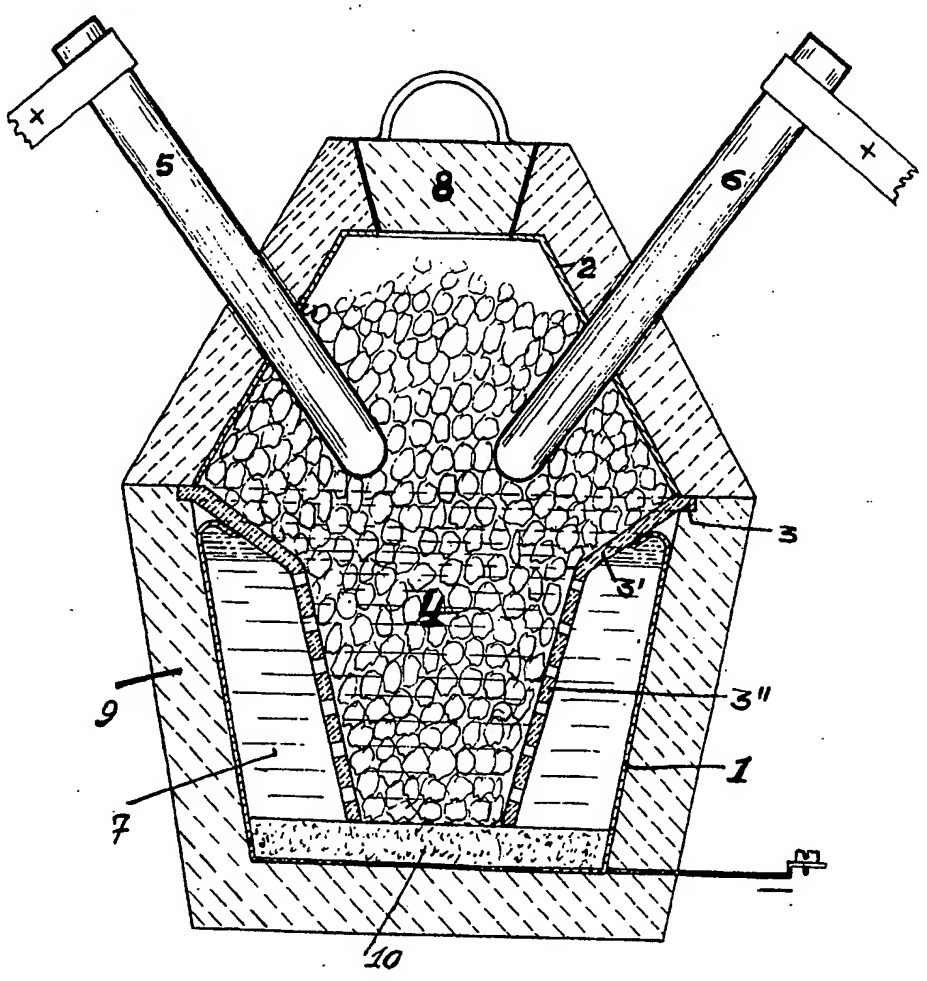
London, W.C.1,
Agents for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1936



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